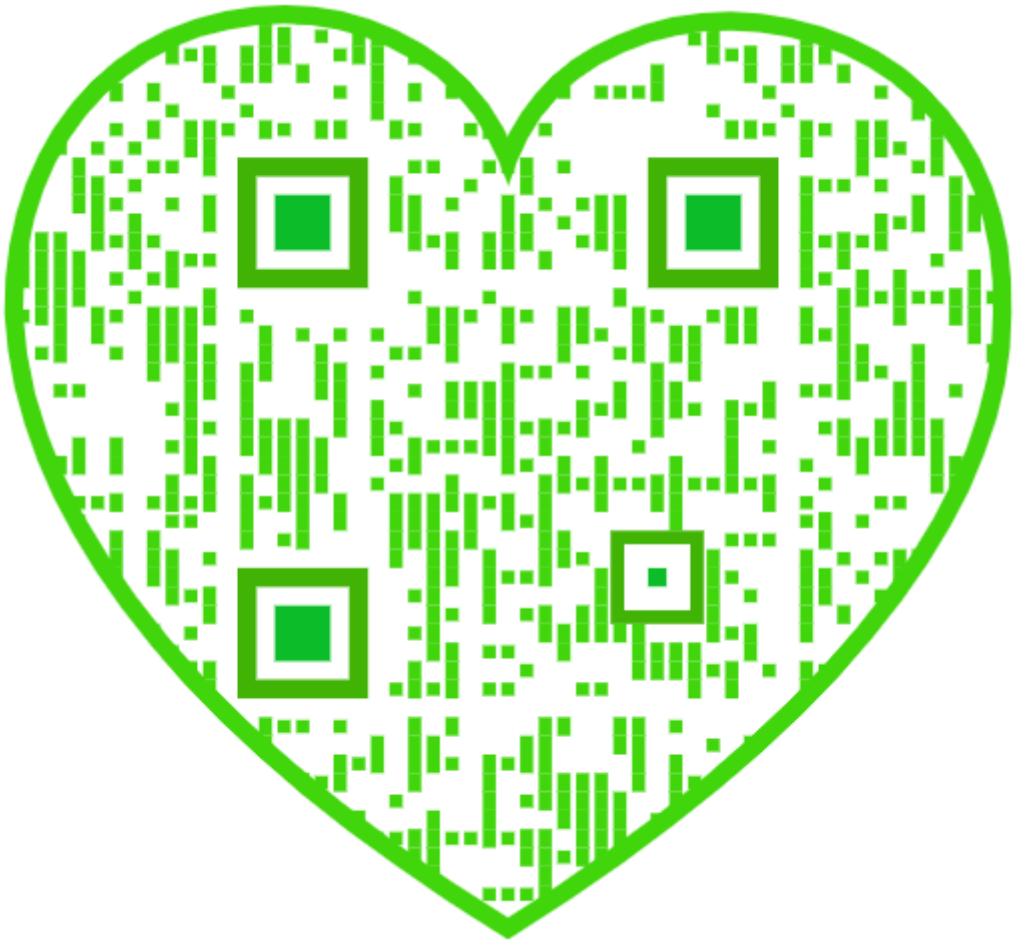

COLLOID CHEMISTRY

AN INTRODUCTION, WITH SOME PRACTICAL APPLICATIONS

BY

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PREFACE

THIS little book is the result of an attempt to compress within a very limited space, the most important general properties of colloids, and some of the practical applications of colloid chemistry. Its object will be accomplished if it is helpful in extending the sphere of interest in this fascinating twilight zone between physics and chemistry.

J. A.

NEW YORK,
Nov. 1, 1918.

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COLLOID CHEMISTRY

CHAPTER I

Introduction

Although many facts and principles concerning colloids have from time immemorial been known and utilized empirically, the scientific foundation of modern colloid chemistry was laid by an Englishman, Thomas Graham, F.R.S., Master of the Mint. In two basic papers on this subject, the first entitled "*Liquid Diffusion Applied to Analysis,*" read before the Royal Society of London, June 13, 1861, the second entitled "*On the Properties of Colloidal Silicic Acid and other Analogous Colloidal Substances,*" published in the Proceedings of the Royal Society, June 16, 1864, Graham pointed out the essential facts regarding colloids and the colloidal condition, and established much of the nomenclature in use at the present day. In the first of these

papers Graham says: "The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol and sulphate of magnesia. But the substances named belong all, as regards diffusion, to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina and other metallic peroxids of the aluminous class, when they exist in the soluble

form; with starch, dextrin and the gums, caramel, tannin, albumen, gelatin, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of this class as colloids, and to speak of their peculiar form of aggregation as the colloidal condition of matter. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as crystalloids. The distinction is no doubt one of intimate molecular constitution.

"Although chemically inert in the ordinary

sense, colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a pectous modification; and they often pass under the slightest influences from the first to the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble

at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition. (H. Rose.) The colloidal is, in fact, a dynamical state of matter, the crystalloidal being the statical condition. The colloid possesses Energia. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element) may the characteristic protraction of chemico-organic changes also be referred. . . .

"It may perhaps be allowed to me to apply the convenient term dialysis to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment, or parchment-paper. . . ."

At the beginning of the second paper above referred to, Graham states: "The prevalent notions respecting solubility have been de-

rived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal solutions." From this it may be seen that Graham appreciated the fact that all the laws of crystalloidal solutions could not be applied to colloidal solutions. In the case of crystalloidal solutions the dissolved substance is present in a state of molecular subdivision, and, according to the ionization theory, is in many cases dissociated into ions. With colloidal solutions, on the other hand, we have a lesser degree of subdivision, and the particles in solution are larger and more cumbersome. As Graham remarked, "The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule." This is to-day the idea generally accepted.

Colloid Chemistry Defined

Colloid chemistry deals with the behavior and properties of matter in the colloidal condition, which, as we now know, means a certain

very fine state of subdivision. While there are no sharp limitations to the size particles in colloidal solutions, it may in a general way be stated that their sphere begins with dimensions somewhat smaller than a wave length of light, and extends downward well into dimensions which theory ascribes to the molecules of crystalloids. (See Table II, p. 12.)

Suspension vs. Solution

With the aid of the ultramicroscope, which renders visible particles approaching in minuteness molecular dimensions, Zsigmondy has shown that there is no sharp line of demarcation between suspensions and solutions, but that with increasing fineness in the subdivision of the dissolved substance, there is a progressive change in the properties of the resulting fluids, the influence of gravity gradually yielding to that of the electric charge of particles, of surface tension and of other forms of energy. Thus in the case of metallic gold, subdivisions whose particles are 1 μ and over act as real suspensions and deposit their gold, whereas much finer subdivisions (60 $\mu\mu$ and under) exhibit all the properties of metal

hydrosols or colloidal solutions. In the ultramicroscope the coarser subdivisions show the well-known Brownian movement, which greatly increases as the particles become smaller, until at the present limit of ultramicroscopic visibility (about 5 $\mu\mu$) it becomes enormous both in speed and amplitude.

On the other hand, there is no sharp distinction between colloids and crystalloids, but as the particles in solution become smaller and smaller, the optical heterogeneity decreases correspondingly, finally vanishing as molecular dimensions are approached.* That even crystalloid solutions are not in a strict sense homogeneous, is indicated by an experiment of van Calcar and Lobry de Bruyn (Rec. Trav.

* In an article entitled "Pedetic Motion in Relation to Colloidal Solutions" published in *Chemical News*, 1892, Vol. 65, p. 90, William Ramsay, Ph.D., F.R.S. (afterward Sir William Ramsay), clearly expressed this view in the following words: "I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion; that the true osmotic pressure has, probably, never been measured; and that a continuous passage can be traced between visible particles in suspension and matter in solution; that, in the words of the old adage, *Natura nihil fit per saltum.*"

chim. Pays-Bas, 1904, **23**, 218), who caused the crystallization of a considerable part of saturated crystalloid solutions at the periphery of a rapidly rotating centrifuge.

CHAPTER II

Classification of Colloids

The broadest classification of colloids is that of Wolfgang Ostwald (Koll. Zeitschr., Vol. 1, page 291), who grouped them according to the physical state (gaseous, liquid or solid) of the subdivided substance (dispersed phase), and of the medium in which the particles of the subdivided substance are distributed (dispersion medium).* Table I (page 11) shows the nine resulting groups and gives some instances of each.

Ostwald's classification, however, is more theoretical than practical, for the properties of colloids are dependent mainly upon the specific nature of the dispersed substance and its degree of subdivision. Following Hardy, Zsigmondy divided colloids into two classes, the *reversible* and *irreversible;* the former redissolve after

* G. Bredig proposed to call colloids "microheterogeneous systems." W. Ostwald called them "dispersed heterogeneous systems," which expression was contracted by P. P. von Weimarn into the term "dispersoids."

desiccation at ordinary temperatures, whereas the latter do not.

TABLE I

Dispersed phase.	Dispersion medium.	Example.
Gas.....	Gas.....	No example, since gases are miscible in all proportions.
Gas.....	Liquid.....	Fine foam, gas in beer.
Gas.....	Solid.....	Gaseous inclusions in minerals (meerschaum, pumice), hydrogen in iron, oxygen in silver.
Liquid.....	Gas.....	Atmospheric fog, clouds, gases at critical state.
Liquid.....	Liquid.....	Emulsions of oil in water, cream, colloidal water in chloroform.
Liquid.....	Solid.....	Mercury in ointments, water in paraffin wax, liquid inclusions in minerals.
Solid.....	Gas.....	Cosmic dust, smoke, condensing vapors, (ammonium chlorid).
Solid.....	Liquid.....	Colloidal gold, colloidal sodium chlorid, colloidal ice in chloroform.
Solid.....	Solid.....	Solid solutions, colloidal gold in ruby glass, coloring matter in gems.

Table II, taken from Zsigmondy,* illustrates this classification, and shows how colloids having the same particle size or degree of subdivision may nevertheless act quite differently because of specific differences in the nature of the dispersed substances.

* Colloids and the Ultramicroscope, J. Wiley & Son, Inc. (Translation by J. Alexander.)

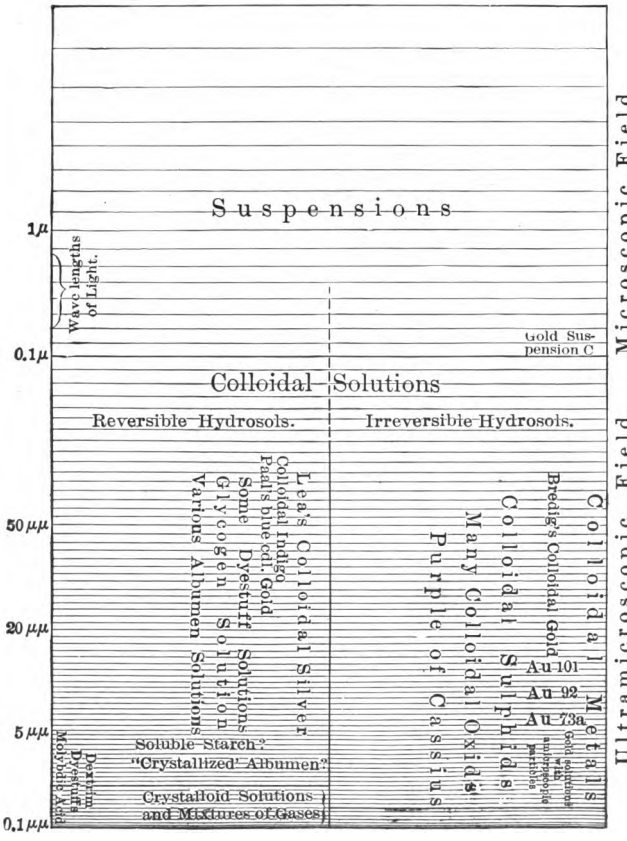
With the reversible colloids (gelatin, gum arabic, albumen), there is a more intimate union between the two phases; in fact it is probable that with them we have really a mixture of (1) a dispersed phase of water subdivided in the solid, with (2) a dispersing phase of the solid finely subdivided in water. The former are therefore called *emulsoids* and the latter *suspensoids*. Colloids of the reversible type are also said to be *hydrophile* or *lyophile*, while the irreversible colloids are *hydrophobe* or *lyophobe*.

No sharp line is to be drawn, however, for besides intermediate or transition cases between the two classes, there may be recognized two groups of irreversible colloids, roughly defined by their behavior upon concentration:

First: The *completely irreversible*, which coagulate while still quite dilute and separate sharply from the solvent with the formation of a pulverulent precipitate rather than a gel (*i.e.*, pure colloidal metals). Chemical or electrical energy is needed to bring them back again into colloidal solution.

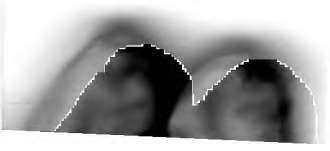
Second: The *incompletely reversible* which, when quite concentrated, form a gel that may

TABLE II



Classification of Colloidal Solutions

according to the size of the particles contained in them and according to their behavior upon desiccation.



be easily redissolved or *peptisized* by comparatively small amounts of reagents, unless the evaporation has proceeded too far (*i.e.*, colloidal stannic acid).

CHAPTER III

Consequences of Subdivision

As the subdivision of a substance proceeds, the area of its effective surface increases enormously, as may be seen from the following Table III adapted from Ostwald. Consequently surface forces, such as adsorption, capillarity and surface tension, become enormously magnified and of primary importance. Furthermore, the so-called radius of molecular attraction (ρ = 50 $\mu\mu$) is well within the colloidal field, so that the specific attractive forces of the particles also enter as a controlling factor. In fact, before substances can unite chemically their particles must be first brought into proper subdivision and proximity,* by solution, fusion, ionization or even by mere pressure, as was demonstrated by W. Spring, who caused fine

* It is a striking fact that absolutely dry sodium is not attacked by absolutely dry chlorin. M. Raffo and A. Pieroni observed that colloidal suphur reduced silver salts energetically, whereas even fine precipitated sulphur did not form silver sulphid in the cold, and did so only partially upon boiling.

TABLE III. RESULT OF PROGRESSIVE DECIMAL SUBDIVISION OF A CUBE

Length of edge.	Number of cubes.	Total surface.
1 cm. = 0.3937 in.	1	6 sq. cm. = 0.93 sq. in.
1 mm. = 0.0394 in.	1,000	60 sq. cm. = 9.3 sq. in.
0.1 mm. = 0.0039 in.	1,000,000	600 sq. cm. = 93 sq. in.
0.01 mm. = 0.0004 in.	1,000,000,000	6000 sq. cm. = 930 sq. in.
1 μ = 0.001 mm.	1,000,000,000,000	6 sq. m. = 212 sq. ft.
0.1 μ = 0.0001 mm.	1,000,000,000,000,000	60 sq. m. = 2,117 sq. ft.
0.01 μ = 0.00001 mm.	1,000,000,000,000,000,000	600 sq. m. = 21,274 sq. ft.
1 $\mu\mu$ = 0.001 μ	1,000,000,000,000,000,000,000	6000 sq. m. = 211,740 sq. ft.
0.1 $\mu\mu$ = 0.0001 μ	1,000,000,000,000,000,000,000,000	6 hectares = 14.83 acres
0.01 $\mu\mu$ = $\frac{4}{10,000,000,000}$ in.	1,000,000,000,000,000,000,000,000,000	60 hectares = 148.26 acres
*0.001 $\mu\mu$ = $\frac{4}{100,000,000,000}$ in.	1,000,000,000,000,000,000,000,000,000,000	6 sq. kilometers = 1482.6 acres = 2½ sq. miles

* These subatomic dimensions approach the theoretical size of electrons

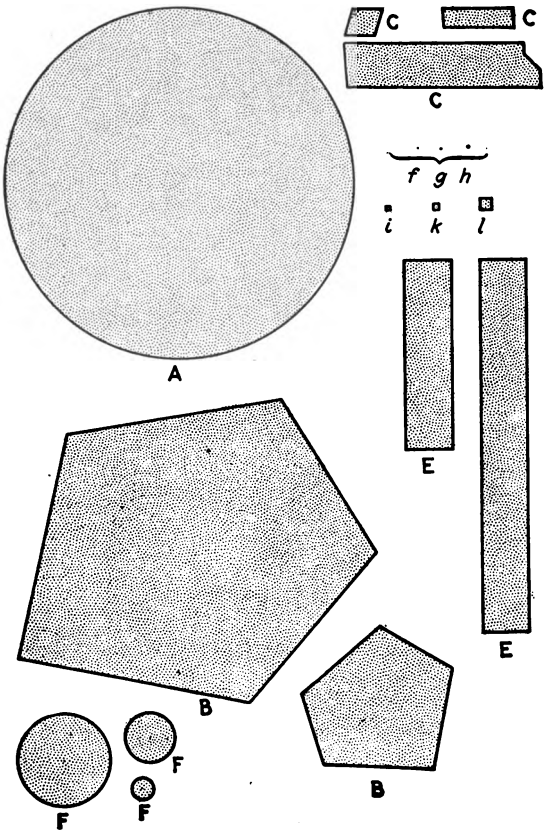
$$1\,\mu = \frac{1}{1,000}\text{ mm.};\ 1\,\mu\mu = \frac{1}{1,000}\,\mu.$$

dry powders to combine chemically by high pressure. If the degree of subdivision is not profound enough to permit of the combination of isolated atoms or ions with each other, chemical combination in the strict sense may not occur, but there may be produced "adsorption compounds" resulting from the union of atomic or ionic mobs in indefinite or non-stoichiometric proportions, under the influence of more or less modified chemical forces. The combination of arsenious acid and ferric oxid which Bunsen regarded as a basic ferric arsenite, 4 Fe_2O_3, As_2O_3, 5 H_2O, has been shown by Biltz and Behre to be an adsorption compound; and Zsigmondy proved "Purple of Cassius" to be an adsorption compound of colloidal gold and colloidal stannic acid by actually synthesizing it by mixing the two separate colloidal solutions.

The effect of increasing subdivision upon the particles in colloidal solutions is illustrated in Table IV, adapted from Zsigmondy. Tables V and VI were prepared by Zsigmondy to illustrate visually the relation of the sizes of colloidal particles to well-known microscopic objects on the one hand and to the theoretical sizes of molecules on the other.

TABLE V

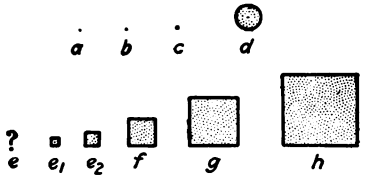
LINEAR MAGNIFICATION 1 : 10,000

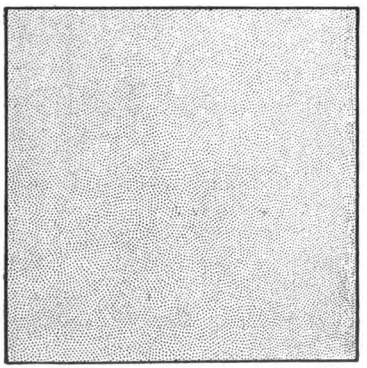


A. Human blood corpuscles (diameter 7.5 μ, thickness 1.6 μ).
B. Fragment of rice starch granule (according to v. Höhnel) 3–8 μ.
C. Particles in a kaolin suspension.
E. Anthrax bacillus (length 4–15 μ, width about 1 μ).
F. Cocci (diameter about 0.5–1 μ, rarely 2 μ).
f, *g*, *h*. Particles of colloidal gold solutions Au_{72}, Au_{22}, Au_{97} (0.006–0.015 μ).
i, *k*, *l*. Particles from settled gold suspensions (0.075–0.2 μ).

TABLE VI

LINEAR MAGNIFICATION 1 : 1,000,000





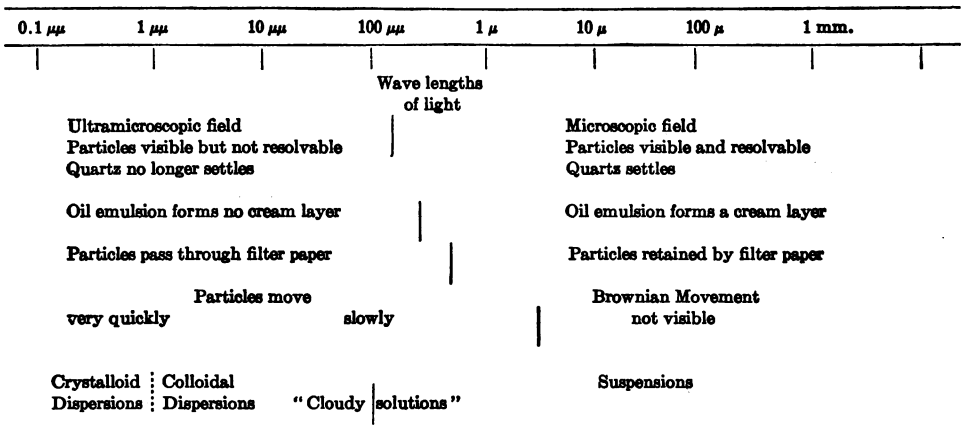
a-d. — *Hypothetical Molecular Dimensions*

a. Hydrogen molecule — dia. 0.1 $\mu\mu$.
b. Alcohol molecule — dia. 0.5 $\mu\mu$.
c. Chloroform molecule — dia. 0.8 $\mu\mu$.
d. Molecule of soluble starch — dia. about 5 $\mu\mu$.

e-h. — *Gold Particles in Colloidal Gold Solutions*

e. Gold particle in Au_{16} (too small to determine).
e_1. " " " " , about 1.7 $\mu\mu$.
e_2. " " " " , " 3.0 $\mu\mu$.
f. " " " $Au_{72\pm}$, " 6 $\mu\mu$.
g. " " " Au_{92}, " 10 $\mu\mu$.
h. " " " Au_{97}, " 15 $\mu\mu$.
i. Gold particle in settled gold suspension.

TABLE IV


0.1 μμ
1 μμ
10 μμ
100 μμ
1 μ
10 μ
100 μ
1 mm.
Wave lengths of light
Ultramicroscopic field
Particles visible but not resolvable
Quartz no longer settles
Microscopic field
Particles visible and resolvable
Quartz settles
Oil emulsion forms no cream layer
Oil emulsion forms a cream layer
Particles pass through filter paper
Particles retained by filter paper
Particles move very quickly
slowly
Brownian Movement not visible
Crystalloid Dispersions
Colloidal Dispersions
"Cloudy solutions"
Suspensions

CHAPTER IV

The Ultramicroscope

As this instrument revolutionized colloid research, a brief description of it is essential.

It is a matter of every-day experience that the unseen motes and dust particles in the air become visible in a beam of bright light, especially against a dark ground, and in this simple fact lies the principle of the ultramicroscope.

Faraday and later Tyndall made use of a convergent beam of light to demonstrate the optical inhomogeneity of solutions; for in fluids not optically clear, the path of the beam becomes more or less distinctly visible, because of the light scattered by the particles present. In this manner can be recognized much smaller quantities of matter than by spectrum analysis — in fact less than 10^{-8} mg. (1/10,000,000) of metallic gold can thus be detected with the naked eye.

Prof. Richard Zsigmondy while experimenting with colloidal solutions conceived the idea of examining this light cone microscopically.

His preliminary experiments having demonstrated that he could thus see the individual particles in various hydrosols, he sought the assistance of Dr. H. Siedentopf, scientific director of the Carl Zeiss factory, in Jena, where was produced the first efficient ultramicroscope.

The ultramicroscope consists essentially of a compound microscope arranged for examining in a dark field an intense convergent beam of light cast within or upon the substance under examination. The light seen by the eye represents, therefore, the light diffracted, scattered or reflected upward by the substance or by particles within it.

If within a thin beam of light from a projection lantern we scatter successively powders of different substances in various degrees of fineness (mica ground to pass 60, 100 and 160 mesh; lampblack; powdered oxid of zinc; flake and powdered graphite), some of them will produce only a homogeneous illumination of the beam in which no isolated particles can be seen, whereas with others, the individual particles are distinctly visible.

Passing the beam through a beaker of dis-

tilled water, nothing can be seen; but upon the addition of a few drops of colloidal gold solution, which appears quite clear to transmitted light, the path of the beam through the fluid immediately becomes visible. This Tyndall effect,* as it is called, might be considered a criterion of colloidal solution were it not that very minute traces of colloidal impurities can produce it and it is often exhibited by solutions generally regarded as crystalloidal — those of many dyestuffs for example; furthermore with increasing fineness of subdivision the Tyndall effect decreases, disappearing as molecular dimensions are approached.

Just as in the cosmic field our most powerful telescopes fail to resolve the fixed stars, which are nevertheless *visible* as points of light of varying brilliancy, so, too, in the ultramicroscopic field, we can *see* particles much smaller than the resolving power of the microscope (that is, smaller than a wave length of light) provided only that they diffract sufficient light to affect the retina. Based upon the experience of astronomers we may be able greatly to increase the sensitiveness of the ultramicro-

* Also known as the Faraday-Tyndall effect.

scope by fortifying the eye, so to speak, with the photographic plate, using at the same time tropical sunlight or ultraviolet light for illumination.

In the original form of the ultramicroscope, as perfected by Siedentopf and Zsigmondy, which is the one best adapted for the examination of transparent solids, a side illumination is effected by a microscope objective with micrometer movements, which throws an intense but minute conical beam of light into the fluid contained in a little cell having quartz windows at the side and top. Above this cell a compound microscope is adjusted vertically, so that the narrowest part of the light cone occupies the center of the focal plane. If the fluid under examination is optically clear or if it contains particles so small that they cannot diffract sufficient light to create a visual impression, the light cone cannot be seen. If enough light is diffracted, the light cone becomes visible, being homogeneous if the particles are too small or too close together to be individually seen, and heterogeneous if the particles can be individually distinguished. Particles or dimensions

beyond the resolving power of the microscope (about $\frac{1}{4}$ μ) are for brevity termed *ultramicrons*. Ultramicrons that can individually be made visible are called *submicrons* (or hypomicrons) while those so small that they produce an unresolvable light cone are termed *amicrons*.

Knowing the percentage of gold present in a colloidal gold solution and assuming a certain specific gravity and uniform shape for the gold particles, the average size and mass of a single particle of colloidal gold can be calculated, if the number present in a given volume be first counted. In this manner Zsigmondy has shown that the smallest particles of colloidal gold which can be individually distinguished with bright sunlight, are approximately 5 $\mu\mu$ in diameter, that is, five-millionths of a millimeter; still smaller particles exist but they produce only an unresolvable light cone. Magnified 1,000,000 times such a tiny gold particle would be about $\frac{1}{4}$ inch in diameter, while a human red blood corpuscle would be about 25 feet across, and a hydrogen molecule a speck barely visible. The gold particles in the unresolvable light cone must therefore

closely approach molecular dimensions. In fact, by allowing amicrons to grow into visibility in a suitable solution and then counting them, Zsigmondy has recently shown that some of the particles of colloidal gold have a mass of $1–5.10^{-16}$ mg., indicating a size of 1.7 to 3 $\mu\mu$.

Various other types of ultramicroscopes, mainly modifications of dark field illumination, have been developed by Cotton and Mouton, Ignatowski (made by Leitz), Siedentopf (cardioid condenser, made by Zeiss) and others, and besides being useful in examining colloidal solutions, they have enabled pathologists to see and discover ultramicroscopic bacteria (spirochetes, infantile paralysis).

Bausch & Lamb Optical Co. of Rochester, N. Y., are now producing a useful ultramicroscope.

CHAPTER V

General Properties of Colloids

The optical properties of colloids and their simulation of chemical compounds have been already referred to. The other general properties of colloids may be considered under the following headings:

1. Colloidal Protection.
2. Dialysis, Ultrafiltration and Diffusion.
3. Electric Charge and Migration.
4. Pectization (Coagulation) and Peptization.

COLLOIDAL PROTECTION. — A most interesting and important fact regarding reversible colloids is that they can communicate their reversible property to irreversible colloids. The addition of gelatin (as little as 0.0001 per cent) to a solution of colloidal gold protects the latter against coagulation upon the addition of electrolytes, and permits it to redissolve after desiccation. Ultramicroscopic examination has shown that the gelatin does not affect the

motility of the gold particles, thus disposing of the suggestion of Lobry de Bruyn that it acts by decreasing their motion. The idea advanced by Müller (Ber., 1904, **37**, 11) that gelatin acts by increasing the viscosity and thus preventing the deposition of suspended particles is disproved by the fact that quince kernel gum, notwithstanding its viscosity, exercises no protective action,* whereas the small quantities of gelatin necessary to produce this effect cannot appreciably increase the viscosity, and actually permit gold particles to settle if they are large enough to do so.

The action of reversible colloids in opposing group formation, is of great technical importance, for in many cases it permits them to hinder, modify and even prevent coagulation, precipitation and crystallization.

Dialysis. — Colloid solutions possess a small but definite diffusibility through colloidal septa (parchment paper, bladder) as was recognized by Graham, who found that "tannic acid passes through parchment-paper about 200 times slower than sodium chlorid; gum arabic

* According to Zsigmondy, quince kernel gum acts as a protector with some substances.

400 times slower." Graham's original form of dialyzer may be made from a wide-mouthed bottle whose bottom has been removed.* The mouth is closed by a piece of bladder or parchment paper tightly bound on, the solution to be dialyzed is poured in, and the bottle immersed about halfway in water contained in a larger vessel. Most of the crystalloids diffuse through the membrane into the outer water, which should be frequently renewed, while most of the colloids remain in the original bottle, and may be thus obtained in a purified condition. Improved modern dialyzers consist of parchment or collodion sacs or thimbles, or even of whole bladders, which have the advantage of a larger dialyzing surface.

ULTRAFILTRATION.—H. Bechhold found that he could make filtering membranes of varying degrees of permeability by forming them from jellies of varying concentration. He used principally collodion dissolved in glacial acetic acid and afterward immersed in water, and gelatin jellies hardened in ice-cold formaldehyde. The jellies were formed and hardened on pieces of filter paper, which were supported from below

* A lamp chimney will answer very well.

by nickel wire cloth, and clamped between two flanges. The liquid to be subjected to ultrafiltration is introduced in the chamber thus formed and forced through the prepared septum by appropriate pressure, which may run up to 20 atmospheres or more and may be produced by a pump or by compressed gas (air, nitrogen or CO_2). Table VII (p. 28), prepared by Bechhold, shows various colloids arranged in order of the diminishing size of their particles in solution, and was obtained by using ultrafilters of varying degrees of porosity or permeability.

By means of ultrafiltration through ultrafilters of appropriate permeability, not only may colloids be separated from crystalloids, but colloids having particles of different sizes may be separated from each other.

DIFFUSION. — Diffusion through a septum is, of course, involved in dialysis. If, however, diffusion occurs *into a jelly*, many interesting phenomena may develop, especially if the jelly adsorbs any of the diffusing substances or contains substances which can react with them.

Owing to the enormous surface they present,

TABLE VII

Suspensions.
Prussian blue.
Platinum sol (made by Bredig's method).
Ferric oxid hydrosol.
Casein (in milk).
Arsenic sulphid hydrosol.
Colloidal gold hydrosol (Zsigmondy's No. 4, particles about 40 $\mu\mu$).
Colloidal bismuth oxid (Paal's "Bismon").
Colloidal silver (Paal's "Lysargin").
Colloidal silver (von Heyden's "Collargol," particles about 20 $\mu\mu$).
Colloidal gold hydrosol (Zsigmondy's No. 0, particles about 1–4 $\mu\mu$).
Gelatin solution, 1 per cent.
Hemoglobin solution, 1 per cent (molecular weight about 16,000).
Serum albumin (molecular weight about 5000 to 15,000).
Diphtheria toxin.
Protalbumoses.
Colloidal silicic acid.
Lysalbinic acid.
Deuteroalbumoses *A*.
Deuteroalbumoses *B* (molecular weight about 2400).
Deuteroalbumoses *C*.
Litmus.
Dextrin (molecular weight about 965).
Crystalloids.

colloidal gels exhibit a powerful adsorptive action. In fact, even when percolated through such a relatively coarse-grained septum as sand, most solutions issue with a materially reduced

content of solute, and benzopurpurin solutions may be thus decolorized. Further, if a solute hydrolyzes into ions having different degrees of adsorbability or different rates of diffusibility, they may be actually separated by diffusion through a colloidal gel.

This phenomenon is nicely exhibited by what may be termed a "patriotic test tube," prepared by filling a tube about two-thirds full with a slightly alkaline solution of agar containing a little potassium ferrocyanid and enough phenolphthalein to turn it pink. After the agar has set to a firm gel, a solution of ferric chlorid is carefully poured on top, and almost instantly the separation becomes evident. The iron forms with the ferrocyanid a slowly advancing band of blue, before which the more rapidly diffusing hydrochloric acid spreads a white band as it discharges the pink of the indicator. After the lapse of a few days the tube is about equally banded in red, white, and blue.

Even then the tubes do not cease to be of interest, for if they are allowed to stand several weeks the pink color is all discharged and there develop peculiar bands or striations of blue, apparently due to the fact that the iron ferro-

cyanid temporarily blocks the diffusion passage, which are gradually opened again after a layer of the blue salt has diffused on from the lower surface.

Not only may ions be thus separated, but if two solutes in the same solvent possess different rates of diffusion or different degrees of adsorbability, they also may be separated from each other by diffusion through a colloidal gel or septum. (Differential Diffusion.)

ELECTRIC CHARGE AND MIGRATION. — The particles of practically all colloidal solutions possess an electric charge, and under the influence of an electric current (difference of potential) move toward the electrode having the opposite charge. (*Electrophoresis.*) In general, when two substances are brought into contact, the one having the *higher* dielectric constant becomes *positively* charged, whereas the one with the *lower* dielectric constant becomes *negatively* charged (Cohen's Law). Since water has a high dielectric constant (80), most substances suspended in pure water become negatively charged and wander to the anode. On the other hand if suspended in oil of turpentine, which has a low dielectric

constant (2.23), they become positively charged and wander to the cathode.

If, however, electrolytes are present, Coehn's law is superseded by other controlling factors, such as the adsorption of ions, which may give their charge to the suspended particles. In fact Hardy found that in pure water albumen was amphoteric; in the presence of a trace of alkali it acquired a negative charge and migrated to the anode; but a trace of acid gave it a positive charge and it then migrated to the cathode. The following table shows the usual charge and migration tendency of a number of *aqueous* colloidal solutions.

Charged + Migrate to Cathode (− Pole)	Charged − Migrate to Anode (+ Pole)
1. Hydrates of Fe, Cu, Cd, Al, Zr, Ce, Th.	1. Sulphids of As, Sb, Cu, Pb, Cd. Halides of Ag.
2. Titanic acid.	2. Stannic acid, silicic acid.
3. Colloidal Bi, Pb, Fe and Cu (Bredig's method).	3. Colloidal Pt, Au, Ag, and Hg, I, S, Se.
4. Albumen, hemoglobin, agar.	4. Gum arabic, soluble starch, gamboge, mastic, oil emulsion.
5. *Basic Dyes:* Methyl violet, Bismarck brown, methylen blue, Hofmann violet.	5. *Acid Dyes:* Eosin, fuchsin, anilin blue, indigo, soluble Prussian blue.

PECTIZATION AND PEPTIZATION. — Briefly stated pectization means the coagulation of a colloidal sol, and peptization its redispersion. If a small quantity of an electrolyte is added

to a pure ruby red colloidal gold solution, the latter changes to a blue or violet color, and deposits its gold as a fine blackish coagulum or precipitate.* By watching in the ultramicroscope the coagulation of very dilute milk by dilute acid, the individual particles of the colloidal casein may be seen to gather gradually together into groups, whose motion becomes progressively less as their size increases, until they are no longer able to stay afloat, and finally coagulate in large grape-like clusters. Hardy believes that the particles of colloids adsorb the oppositely charged ions of electrolytes present; at the *isoelectric point* (that is when there is no excess either of positive or negative charges on the particles) coagulation occurs. If, however, an *excess* of electrolyte be added *all at once*, the isoelectric point may be passed before coagulation occurs, and the particles acquire a charge opposite to the one they had originally. Under such conditions, no coagulation may result.

* The amount in milligrams of protective colloid just sufficient to prevent the change to violet of 10 cc. of bright red colloidal gold solution by the addition of 1 cc. of a 10 per cent solution of NaCl, is called the "gold figure" or "gold number" of the protector.

Burton epitomizes the difference in action of various electrolytes as follows: "Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends entirely on the ion bearing a charge of sign opposite to that of the colloidal particle; and, second, with solutions of salts, trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the latter, in turn, much greater than univalent. Acids and alkalis in particular cases act more strongly than the corresponding salts."

High-tension electric discharges may also effect the coagulation or precipitation of a finely subdivided or dispersed phase; which fact was utilized by Sir Oliver Lodge in dispelling fogs, and by Cottrell in coagulating smelter and similar fumes.

PEPTIZATION. — So strong is the analogy between digestion and colloidal disintegration that Thomas Graham, the father of colloid chemistry, coined the word *peptization* to express the liquefaction of a gel. He first speaks of the coagulation or pectization of

colloids. "The pectization of liquid silicic acid," he states, "and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may be again liquefied, and have its energy restored by contact with very moderate amounts of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100 degrees. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids in such circumstances may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure

jellies of alumina, peroxide of iron and titanic acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid."

Peptization is in reality deflocculation, a dispersion of groups into separate particles which once more acquire active motion and remain afloat or in solution. The detergent action of soap and dilute alkalis is due to the fact that they deflocculate adhering particles of "dirt."

CHAPTER VI

Practical Applications of Colloid Chemical Principles

The practical applications of colloid chemistry are so manifold and widespread that they touch every branch of science and technology. Whole books may be and have been written on many of the most restricted fields, while the scientific literature teems with monographs and articles, directly on, or applicable to, colloid-chemical subjects. In what follows, it will be possible therefore to give not an exhaustive, but only a most general survey, intended rather to show the ubiquity of colloid phenomena; and many important topics must be dismissed with a most rudimentary discussion, altogether incommensurate with their importance.

Astronomy. — As matter in colloidal state is so common on our relatively minute earth, it is but natural to expect to find many instances of colloidal dispersion in the immensity of the Universe.

Cosmic dust is widely distributed throughout space, and as it is gathered up by the superior attraction of the larger heavenly masses (suns, planets, etc.), which in any system grow at the expense of the smaller masses, fresh quantities are continually produced by the collisions of bodies in space, as well as the disintegration of meteorites, comets, asteroids, etc.

The tails of comets seem to consist almost entirely, and the nuclei and coma largely, of colloidally dispersed matter. The great comet of 1882 which made a transit of the sun, was invisible against the solar disc (a position corresponding to attempted observation of colloidal particles in the ordinary microscope against a luminous background), but became visible again after passing beyond the sun's disc (a position corresponding to successful observation of the same colloidal particles in the ultramicroscope against a dark background, the eye of the observer being protected from the source of illumination).

The streaming of the cometary tails away from the sun may be due to the ionization of the constituent colloidal particles, and their consequent electrical repulsion; or more prob-

ably, it may be due to the sun's rays, as was pointed out by J. Clerk Maxwell. The intensity of the action of the sun's rays on a particle depends upon its *surface*, which varies as the *square* of its diameter, whereas the gravitation of the same particle to the sun depends upon its *mass*, which varies as the *cube* of its diameter. Theoretically in the case of a particle whose density equals that of water, the repulsion balances gravitation when the diameter reaches 0.0015 mm. (= 1.5 μ). As the diameter diminishes the repulsive force gains the ascendancy, soon reaching a maximum and again diminishing, until when the particle has a diameter of only 0.00007 (= 70 $\mu\mu$) the two forces again balance each other.*

These figures, which refer to a substance having the density of water, are approximately of colloidal dimensions; but in the case of denser bodies the subdivision would be even more profound. It is therefore not surprising that, when the earth recently passed through the tail of a comet, no disturbance of any kind was

* See Simon Newcomb's article on "Comet," *Encyclopedia Britannica*, 11th edition. Also Svante Arrhenius, "Worlds in the Making," Harper & Bros.

noticed. The comet's tail is a vast celestial camouflage — its luminosity a macroscopic Faraday-Tyndall effect.

The nebulæ, too, apparently consist of finely dispersed matter, rendered luminous by neighboring suns; although with them as with the comets, a small part of the light may result from self-luminescence (incandescent gas, etc.).

METEOROLOGY. — What we commonly call "weather conditions" are largely dependent upon the degree of dispersion of water in the atmosphere, and this dispersion is mainly effected and maintained by solar heat and electrical energy. When air carrying water vapor is chilled by rising to a higher level, meeting a colder mass of air, or even by the alternation of night and day, the moisture it contains assumes the colloidal state as cloud, fog or mist; and as the coagulation of the dispersed water proceeds, these in turn may condense still further into dew, rain, snow or hail, depending upon conditions. When the dispersed water aggregates, there is naturally set free the energy originally used in its dispersion, and this may appear as electricity (lightning) especially if the aggregation occurs

suddenly as is the case in thunder and hail storms. We have all noticed how a nearby lightning flash is promptly followed by an increased fall of raindrops.

Were it not for our atmosphere, the sun would appear to us like a fiery ball set in a black star-sprinkled sky. The blue color of the sky is due to diffraction of the sunlight by the earth's atmosphere, a gigantic Tyndall effect. If we look edgewise through a clear sheet of glass, we at once notice the green color due to colloidally dispersed iron, and in like manner, if we look through a great length of the atmosphere the prevailing color is blue. As the poet Campbell beautifully puts it:

> "'Tis distance lends enchantment to the view,
> And robes the mountain in its azure hue."

After the tremendous explosive eruption of the volcano Krakatoa in 1883, colloidal dust and ashes were projected so high that they gradually spread around the earth, causing "golden sunsets."

We do not know to what extent electrical conditions on the earth affect the dispersion of substances in its atmosphere; but since half of the earth is always heated by the sun while

the other half is cooler, thermoelectric currents are continually circulating about the earth. Variations in solar radiation due to sun-spots and the like, cause violent electric and magnetic storms which are intimately connected with the aurora, and other atmospheric phenomena (ionization, electrical charge of dispersed particles); and it is well known that sun-spots exercise a potent influence on the weather.

GEOLOGY AND MINERALOGY. — The ordinary properties of the solid constituents of the earth's crust depend more upon their state of physical subdivision than upon their chemical constitution. Atterberg classified the fragments of minerals and rocks as follows:

	Diameter.
Boulders	2 m. to 20 cm.
Pebbles	20 cm. to 2 cm.
Gravel	2 cm. to 2 mm.
Sand	2 mm. to 0.2 mm.
Earth	0.2 mm. to 0.02 mm.
Loam	0.2 mm. to 0.002 mm.
Clay	smaller than 0.002 mm.

The smaller the particles, the greater their capillarity and the ease with which they are moved by wind and by water, but the less their permeability to water. Fine defloccu-

lated clay is carried thousands of miles by rivers until it is finally coagulated by the salts of the ocean, as may be observed in the deltas of the Ganges, Nile and Mississippi. Fine particles are easily cemented by pressure or igneous action into rocks (*e.g.*, sandstone, slate), or may act as a cement for large particles (*e.g.*, pudding-stone) or as a matrix for fossils.

Many minerals are themselves colloidal gels (*e.g.*, opal, flint, bauxite) or result from the weathering of other minerals with consequent gel formation (*e.g.*, kaolin from kaolinite, serpentine from diabase). Most gems owe their colors to impurities colloidally dispersed within them (*e.g.*, ruby, emerald, amethyst). Dendrites are formed by solutions diffusing through mineral gels. Colloidal minerals usually adsorb, and are dyed by aniline dyes (methylen blue), whereas crystalloid minerals are unaffected.

Clay and Ceramics. — The effect of vegetable extractive matters on the working properties of clay have been known from ancient times — in the Bible (Exodus V) it is mentioned that brick cannot be made with-

out straw. Recently patents have been taken out for "Egyptianizing" clay by adding to it tannin, extract of straw, humus and the like. Glue and similar protective colloids deflocculate or "free out" clay and make it "cover" in paper-coating and kalsomining. The working properties of clays depend largely upon the size of their constituent particles and their state of aggregation. This is especially evident in ceramics. Articles molded of clay and then burned, lose their hydrosol condition and become hardened into pottery.

AGRICULTURE. — Although from time immemorial farmers have classified soils on the basis of their physical and physiological character as "light" or "heavy," "rich" or "poor," "productive" or "unproductive," etc., it is only within comparatively recent years that chemists have begun to realize the full importance of the rôle played by the colloids, especially the organic colloids of the soil.

Many important properties of soils, such as permeability, capillarity, absorption, moisture content, etc., are dependent not so much upon the chemical composition as upon the size of

the constituent soil particles. (See Atterberg, Schwed, landw. Akad., 1903, and Chem. Zeit., 1905, **29**, 195; Patten and Waggaman, U. S. Dépt. of Agri. Bureau of Soils, Bull. No. 52, 1908). In coarse sand, for example, the amount of water is greatest at the bottom and smallest at the top, whereas in fine clay the distribution is much more uniform.

Among the natural agencies tending to increase the size of the minute soil particles may be mentioned heat with its drying or evaporative effect, freezing, and the coagulating or flocculating action of soluble inorganic salts and some organic substances present in the soil. On the other hand, included in that little known class of substances vaguely described as "humus," there are numerous organic substances derived from the bacterial, plant, or animal débris, or exuded by the roots of plants, which act as protective colloids (Schutzkolloide) and tend to produce and maintain the hydrosol, or deflocculatd condition. (See P. Ehrenberg, "Die Kollide des Ackerbodens," Zeits. angew. Chem., 1908, **41**, 2122.) In an excellent paper on the mechanics of soil moisture, L. J. Briggs (U. S.

Dept. of Agric., Bureau of Soils, Bull. No. 10, 1897) pointed out that very small quantities of certain organic substances, such as are continually being produced in the soil by the decay of organic matter, greatly decrease the surface tension of solutions, thus counteracting to a large extent the effects of the surface application of soluble salts which would tend to draw moisture to the surface by increasing the surface tension of the capillary water of soils. It is well known, however, that an excess of salts will ruin a soil physically, as is evident after flooding by sea water or the excessive application of chemical fertilizers. Of interest in this connection is the recent work of the Bureau of Soils, U. S. Department of Agriculture, carried out by Cameron, Schreiner, Livingston and their co-workers. Thus plants grown in the unproductive Takoma soil, were greatly benefitted by green manure, oak leaves, tannin and pyrogallol. The injurious effects of quinone and some other organic substances may be due to their ability to precipitate or flocculate the protective colloids of the soil; for as Lumière and Seyewetz have shown (Bull. Soc. Chim.,

1907, **4**, 428–431; J. S. C. I., 1907, 703) quinone renders gelatin insoluble.

The fact observed by Fickenday (J. Landw., 1906, **54**, 343) that more alkali is required to flocculate natural clay soils than kaolin suspensions, he attributes to the protective action of the humus present (see Keppeler and Spangenberg, J. Landw., 1907, **55**, 299).

A. S. Cushman, in his excellent work upon the use of feldspathic rock as fertilizer (U. S. Dept. of Agriculture, Bureau of Plant Industry, Bulletin No. 104; Cushman and Hubbard, J. Am. Chem. Soc., **30**, 779), has shown that the fine grinding of feldspar increases the amount of potash available under the action of water. Thus, a coarse powder having an area of 43 sq. cm. per cc. of solid feldspar yielded 0.013 per cent, whereas a fine powder whose area was 501,486 sq. cm. per cc. yielded 0.873 per cent of potash and soda. These fine particles averaged about 0.1 μ in diameter, which is relatively large as compared with colloidal dimensions; but under the action of physical and chemical soil agencies they undergo further disintegration, finally reaching a colloidal condition in which still more of

their potash is available, a condition favored and maintained by the organic protective colloids of the soil.

With these brief and inadequate remarks we must dismiss this subject of such vast importance and fascinating interest, referring to the extensive literature, much of which is quoted in Bulletin No. 52 and the other publications of the Bureau of Soils.

ELECTROPLATING AND ELECTRODEPOSITION OF METALS. — The addition of protective colloids to electroplating baths tends to the production of fine-grained non-crystalline deposits. A. G. Betts in a paper entitled "The Phenomena of Metal Depositing" (J. Am. Electrochem. Soc., 1905, **8**, 63) has shown that there are many factors influencing the action of the colloid, and has suggested a number of possible explanations. The correct explanation, however, has been given by Müller and Bahntje (Z. Elektrochem., 1906, **12**, 317; J. S. C. I., 1906, 484) who state that the added colloid keeps the deposited metal (copper) in an amorphous, non-crystalline condition, gelatin producing the most powerful effect, egg albumen considerably less, while gum and

starch have comparatively little action. They also found that the deposited copper weighed about 0.2 per cent more than under normal conditions, indicating that some of the colloid had been carried down with the metal.

The relative efficiency of the colloids just referred to corresponds to their relative efficiency in protecting from coagulation solutions of colloidal gold (see Zsigmondy, J. S. C. I., 1902, 192; also Colloids and the Ultramicroscope, p.. 81), which is additional evidence that we have another instance of protective colloidal action, by which the crystallization forces of the metal are powerfully influenced.

METALLURGY. — Since coarsely crystalline metals are brittle, tending to split along the lines of crystal cleavage, various physical and chemical means are employed in technical practice to obtain a hard, fine-grained structure. (See I. Langmuir, Iron & Steel Inst., Sept. 1907; J. S. C. I., 1907, 1094.) Among the physical methods are chilling and rolling, while the chemical methods involve the removal of undesirable constituents (as in the conversion of pig iron into steel) or the addition of desirable constituents (as in the case-

hardening and the manufacturing of "chrome steel," "nickel steel," etc.). For example, P. Putz has shown (J. S. C. I., 1907, 614) that the predominant effect of vanadium in steel is to decrease the size of the ferrite grains and make the material tougher; it renders the ordinary structure due to pearlite fine-grained and homogeneous (see also Beilby, Proc. Roy. Soc. A., **79**, 463; J. S. C. I., 1907, 926).

Now, while the question is one of very great complexity, many of the facts at present available seem to indicate that one of the causes favoring the fine-grained structure is the inhibition of crystallization by substances colloidally dissolved in the molten mass. Thus part of the carbon in iron and steel exists in the graphitic form, and as graphite is slightly soluble in iron (see C. Benedicks, Metallurgie, 1908, **5**, 41; J. S. C. I., 1908, 406); some of it will, under proper conditions, be found in colloidal form (Carnegie Research Reports, J. S. C. I., 1908, **27**, 570; F. Wust, J. S. C. I., 1907, **26**, 412; Hersey, J. S. C. I., **27**, 531). Besides metals may dissolve each other and other substances colloidally, but in the case of ordinary metals this is not easy to demonstrate.

An observation recently made by J. Alexander * is of interest here. Moissan (Comptes rend., **144**, 593, J. S. C. I., 1907, 413) has noted that the addition of a little platinum to metallic mercury causes the latter to "emulsify" in water. Upon making up such an "emulsion," Alexander noticed that the supernatant fluid remained turbid upon standing, and therefore examined the fluid in the ultramicroscope, which revealed the presence of colloidal metallic particles in active motion.

DYEING. — The difference between a physical mixture and a chemical compound is frequently illustrated by dissolving out the sulphur from a *mixture* of iron filings and sulphur dust, and showing that the solvent, carbon bisulphid, does not affect the *compound*, ferrous sulphid. That in many cases dyeing is due, not to chemical combination, but to an adsorption † of the dye by the colloidal fiber, is evident from the fact that some dyestuffs can be extracted from the dyed fiber by means of alcohol. Investigation has shown that many

* J. S. C. I., 1909, **28**, 280.

† In some cases adsorption may be followed by undoubted chemical combination.

dyes are colloidal in solution, and the selective coloring of various fibers, tissues, cells, nuclei, etc., is probably due to selective adsorption or precipitation of one colloid by another. The ultramicroscopic researches of N. Gaidukov (Zeitsch. f. angew Chem., **21**, 393) support this view.

The phenomena of dyeing are rather numerous and complicated, for the dyestuffs are numbered by thousands, and the various fibers, tissues, etc., such as cotton, silk, wool, linen, jute and straw, all react characteristically. In some cases the colloid fiber adsorbs the dye, as with basic colors which dye silk and wool directly; in other cases there is necessary a mordant which is first adsorbed and then fixes the color. Certain colors mutually precipitate each other and may in fact serve as mordants for each other, *e.g.*, methylen blue and dianil blue 2 R.; patent blue V and magenta.

Colloid chemistry also throws much light upon many obscure points in the practical art of dyeing. It is possible to obtain much more level colors in old dye liquors than in fresh ones, and here it seems that colloidally dissolved substances are responsible, exercising

a restraining action upon the absorption of the color. The addition of Glaubers' salt facilitates level dyeing, probably by its action as an electrolyte, producing a partial coagulation of the dyestuff, so that the particles of the latter, thereby made larger, are absorbed more slowly and evenly.

SOAP. — In a comprehensive paper entitled "Modern views on the constitution of soap" (see J. S. C. I., 1907, **26**, 590) Lewkowitsch epitomizes the views of Merklen substantially as follows: "Commercial soap is a product having an essentially variable composition dependent upon (1) the nature of the fatty acids, (2) the composition of the 'nigre' (in the case of settled soaps), (3) the temperature at which the boiling is conducted; it behaves like a colloid and should not be regarded as a compound of sodium salts of fatty acids, with which a definite amount of water is combined chemically, but rather as an 'absorption-product' whose composition is a function of the environment in which the salts of the fatty acids happen to be at the moment of the finishing operations."

Merklen's views conflict with the views as to

the chemical composition of soap previously advanced by Lewkowitsch, who states, in conclusion: "But whatever may be the outcome of renewed experiments, Merklen's views cannot fail to stimulate further research into the composition of soap, and thus help to raise the industry of soap-making, which has too long been looked upon as a mere art, to the rank of a scientifically well-founded industry, the operations of which are governed by the laws of mass action, the phase rule and the modern chemistry of colloids."

The colloidal nature of soap solutions is indicated by their turbidity and their gelatinization. That the detergent action of soap is consequent upon its deflocculating effect was brought out in the interesting Cantor Lecture of H. Jackson (J. Soc. Arts, **55**, 1101 *et seq.*), who examined microscopically the supernatant fluid resulting from washing a dirty cloth with soap and water, and found in it countless particles in a state of oscillatory motion ("pedesis"). When an individual fiber was bathed in soap solution, the dirt particles gradually loosened and began to oscillate; upon substituting salt solution for the soap,

the particles flocculated and the motion ceased. An ultramicroscopic examination of the detergent effects produced by soap should prove of interest.

In this connection mention must be made of the excellent paper of W. D. Richardson on "Transparent Soap" (J. Amer. Chem. Soc., **30**, 414), which he terms a supercooled or supersaturated solution, having distinctly crystalline tendencies and exhibiting colloidal properties. Having in mind the fact that the salts of the higher fatty acids dissolve in water as colloids, and in alcohol as crystalloids (S. Ya. Levites, Zeits. Chem. Ind. Kolloide, **2**, 208, *et seq.*, J. S. C. I., 1908, 1134; Mayer, Schaeffer, and Terroine, Compt. rend., **146**, 484) and also the fact that the alcohol or equivalent solvents (glycerol, sugar, etc.) are used in transparent soap, it seems probable that the crystals which frequently form in it are due to the slow separation of such part of the soap as is in crystalloid solution. This view is supported by the fact adduced by Richardson (loc. cit., p. 418) that the fatty acids separated from the crystals had a higher melting point than those separated from the

clear matrix. The isolation of the crystals was difficult because of their ramifying tendency, which recalls some of the crystal figures exhibited by some mixtures of crystalloids and colloids. What may be called the crystalloid phase of soap is apparently governed by the same factors as those which Tamman has pointed out as governing the crystallization of supercooled solutions, *i.e.*, 1st, the specific power of crystallization; 2nd, the speed of crystallization; 3rd, the viscosity (see Zsigmondy, Colloids and the Ultramicroscope, p. 128 *et seq.*). Thus, gold ruby glass when quickly cooled (or supercooled) is colorless, but acquires a red color upon reheating to the softening point. By ultramicroscopic examination Zsigmondy showed that the nuclei of metallic gold, which in the colorless glass were amicroscopic, grew into ultramicroscopic visibility in the red glass. It therefore seemed to the author that a most important factor in determining the transparency of transparent soap would be the speed of cooling, and some experiments were made along this line.

A piece of commercial transparent soap was melted and cast into two cups, one of which

was quickly chilled in ice, while the other was allowed to cool slowly by immersion in hot water. The quickly cooled piece was transparent, while the other was practically opaque, and showed upon ultramicroscopic examination much larger ultramicrons than the transparent piece.

After standing three or four months, the quickly cooled soap was still transparent to the naked eye, whereas large opaque spots could be seen in the slowly cooled piece. In the ultramicroscope the former appeared as before, whereas the latter showed large and perfectly resolvable crystals in a clear matrix.

These experiments give us an inkling as to what occurs during the "heat treatment" and tempering of metals, and it is to be hoped that some technique may be devised that will give us even a clearer insight than does "etching," into the changes that occur in metals in metallurgical operations (heat treatment), use, age, and even "disease" (tin for example).

Milk. — From a colloid chemical standpoint, the main constituents of milk may be classified as follows:

In crystalloid dispersion { salts (such as NaCl, etc.) sugar (lactose).
In colloidal dispersion { casein — an unstable or irreversible colloid. lactalbumin — a stable or reversible colloid.
In suspension* milk fat.

Most formulas and recipes for modifying cows' milk for infant feeding, and for that matter, many analyses, combine the percentages of lactalbumin and of casein under the collective title of "total proteids," thereby obscuring the highly important fact that the lactalbumin stabilizes and protects the casein from coagulation by acid and rennin.†

The subjoined table will show how milks are influenced by a difference in the ratio between the casein and lactalbumin.

AVERAGE COMPOSITION

Kind of milk.	Casein.	Lactalbumin.	Fat.	Behavior with acid.	Behavior with rennin.
Cow.....	3.02	0.53	3.64	Readily coagulates.	Readily coagulates.
Woman.....	1.03	1.26	3.78	Not readily coagulated.	Not readily coagulated.
Ass.....	0.67	1.55	1.64	.....	.....

* It is probable that some of the fat is in colloidal dispersion.

† See Alexander and Bullowa, Jour. Am. Med. Assoc., Vol. LV, p. 1196 (Oct. 1, 1910).

It is interesting to note that the milks in the above table are arranged in order of their digestibility, which also corresponds with their relative colloidal protection. Thus Jacobi has stated that asses' milk has always been recognized as a refuge in digestive disorders in which neither mother's milk nor cow's milk or mixtures were tolerated.

The addition of protective colloids to cows' milk stabilizes it and makes it act more like mother's milk when treated with acid and rennin. In fact, if sufficient protective colloid be added, coagulation of the casein in the stomach may be entirely prevented, or at least the coagula kept in a very fine state of subdivision.

The action of protective colloids is beautifully illustrated in the ultramicroscope, which enables us to see the individual particles of cows' casein in active motion and watch the course of their coagulation by acid, first into small and then into larger and larger groups, whose motion decreases as their size increases, until finally they sink out of solution in coagulated masses. If, however, some gelatin or gum arabic solution be added to the cows'

milk before the addition of the acid, the casein particles continue their active dance and do not coagulate. In this connection it is interesting to note that the casein particles in mother's milk appear to be much smaller than those in cow's milk, probably because of the more highly protective medium in which they are formed and exist.

Although their method of action was not perfectly understood, protective colloidal substances have for years been used in the modification of cow's milk for infants. For over thirty years Jacobi has advocated the addition of gelatin and gum arabic to cow's milk and infant's diet, and the use of gruels, dextrinized starch and similar reversible colloids is familiar to all. It is interesting to note that sodium citrate, which is largely employed as an addition to cow's milk, acts as a protective colloid, and when going into solution actually exhibits actively moving ultramicrons in the ultramicroscope, a fact which indicates its colloidal condition.

In addition to stabilizing the casein, protective colloids in milk have a very important influence on the milk fat. In the first place

is to be considered the emulsifying and emulsostatic action of reversible colloids. Of much greater importance, however, is the result of stabilizing the casein, for insufficiently protected casein in curding carries down mechanically most of the milk fat present, yielding a greasy, fatty curd which is very difficult for the digestive juices to dissolve.

Ice Cream. — It is a fact well known to practical ice cream makers, and amply proven by experience, that ice cream made without eggs, gelatin or some similar colloidal ingredient, is gritty, grainy or sandy, or else soon becomes so upon standing; whereas ice cream made with small quantities of colloids possesses that rich, mellow, velvety texture so much in demand. Here the added colloid acts as an inhibitor of crystallization or practically speaking as a preserver of texture. The added colloid, especially gelatin, which is the one most frequently used, also serves as a protective colloid in preventing the coagulation of casein, apparently an irreversible hydrosol and a normal constituent of ice cream. In view of what has been said above, it is evident that gelatin thus renders ice cream more digestible.

A very misleading impression is given by some official food chemists referring to gelatin in ice cream as a "filler," which naturally leads to the idea that it is an inferior ingredient added in quantity to cheapen the product. But as gelatin is expensive and as but ½ per cent is used, such a view is evidently erroneous. The food value of gelatin as a protector of the body's nitrogen being generally admitted, and its effect in milk being very beneficial from a digestive point of view, its use in ice cream in the quantities referred to is necessary, legitimate and scientific.

CONFECTIONARY. — In gum drops, marshmallows, "moonshine" and other candies, use is made of gum arabic, gelatin, albumen, and other colloids to prevent the crystallization of the sugar. Thus, besides adding to the food value, they give the candy a smooth and agreeable taste, and preserve it in saleable condition.

BREWING. — Beer contains dextrin and albumin, both colloids. In the brewing process many factors appear which tend to coagulate the albumen. The influence of solid surfaces is illustrated by changing the walls of the

fermenting vessel. Thus a certain wort fermented in glass or enameled vessels showed 0.2450 per cent of albumen; the same wort fermented in a paraffin-lined vessel showed 0.1925, and in a vessel lined with pitch only 0.1750 per cent of albumen. Old-fashioned brewers would never use any vessel unless it had first been treated with a decoction of malt kernels and nut leaves, or else with "fassgelager" (barrel dregs) which acts like the so-called "bierstein," a deposit consisting chiefly of organic substances that forms upon new surfaces and protects albumen from coagulation by their influences.

The influence of fluid surfaces is evident from the fact that in the chemical analysis of beer, benzine, benzol, chloroform, etc., may be used to coagulate and shake out the beer colloids.

The formation of gas bubbles tends to coagulate the dissolved albumen, and this fact killed the so-called "Vacuum Fermentation Process." The jarring due to transportation or even to passing trains may have a deleterious effect. A slight trace of acid tends to stabilize the albumen as do the tannin and

resins from the hops, the dextrins from the mash and the inorganic colloids of calcium and magnesium. A proper balance between the dextrin and albumen is necessary for the formation of a lasting foam and a desirable "body" (Vollmündigkeit).

In America where beer is served icy cold, the chilling produces cloudiness, consequent upon a coagulation of albumen. This was cleverly overcome by Wallerstein, who introduced a proteolytic enzyme which increases the degree of dispersion of the albumen and thus prevents the clouding.

TANNING. — The skins of animals (hide) constitute an organized colloid jelly, formed of bundles of fine fibrils, about 1 μ in diameter, bound together by a cementing material of similar chemical composition, which is largely removed by the liming and other treatment, preceding the tannage proper.

When the swollen hide is placed in the acid tannin solution* (tan liquor), the tannin is powerfully adsorbed by the fiber and combines with it to form leather. It is still a moot

* In alkaline solution both the tannin and the hide are negatively charged and no tanning occurs.

question whether the combination is "physical" or "chemical," but since the fixation of the tannin follows an adsorption isotherm and is reversible in the presence of alkalis, it may justly be called a "colloid combination" which partakes of the nature of both. The positively charged hide and the negatively charged tannin mutually coagulate each other. Gelatin when neutral and free from electrolytes does not precipitate pure tannin, but in acid solution it takes a positive charge and is tanned. The tanning process may be aided electrically by giving the hide a suitable potential, positive in the case of tannin and negative in the case of chromium compounds.

RUBBER. — Rubber is made by coagulating the milky juice (latex) of various plants. Rubber latices are emulsions stabilized by protective colloids (proteins or peptones) and the nature of the coagulant depends upon the nature of the protector. Thus, formaldehyde preserves latices whose protectors are proteins, but coagulates *Kickexia* latex by precipitating the protective peptones.

Vulcanization consists of the combination of sulphur with rubber. At first the sulphur

is adsorbed; and then by heating, part of it enters into a close combination, probably true chemical combination.

PHOTOGRAPHY. — The photographic plate owes its sensitiveness to an "emulsion" of colloidal silver halides stabilized by a protective colloid (gelatin, albumen or collodion). The degree of dispersion is controlled by the conditions of precipitation of the silver salt and the subsequent treatment of the emulsion (ripening). The latent image formed upon the exposure of the plate to light is probably an adsorption compound between colloidal silver and the silver halides.

BOILER SCALE. — In addition to containing various salts intended to precipitate scale-forming ingredients, most formulas for "boiler-compounds" and scale-preventing mixtures include such substances as glue, dextrin, starch, potatoes, tannin, extract of hemlock, etc. These colloids undoubtedly prevent the formation of hard crystalline scale, either by inhibiting to some extent the precipitation of the scale-forming salts or by keeping the precipitate in an extremely fine non-crystalline condition.

CEMENT, MORTAR AND PLASTER. — When freshly mixed, cement and mortar contain colloidal sols or gels, which gradually coagulate or "set" and bind the crystalline elements of the plaster into a coherent whole.

The setting of the plaster of Paris is delayed by glues, gums and other colloidal substances, and "retarders" of this character have been in use for years. On preparing some microscope slides with a mixture containing equal parts of plaster of Paris and water, to which had been added varying proportions of gelatin, the following results were observed:

Per cent gelatin.	Time to set in minutes.	Microscopic appearance of slide.
0	40	Characteristic interlacing crystals of calcium sulphate.
$\frac{1}{100}$	50	No true crystals except in a few spots, where some colloid-free solution had diffused out. Elsewhere aborted sphero-crystals.
$\frac{1}{10}$	260	No true crystals.
$\frac{1}{4}$	910	No true crystals.
$\frac{1}{2}$	960	No true crystals.
1	Not set in 48 hours.	No true crystals.
2	Not set in 48 hours.	No true crystals.

FILTRATION. — Successful filtration depends upon the use of a septum or filtering medium,

whose pores or orifices are small enough to hold back the particles it is desired to separate from the fluid; or the pores may become small enough by the deposit upon or in them of some of the precipitate, or of some added material, such as paper pulp, kieselguhr or shredded asbestos. It is, therefore, evident that the presence of protective colloids, by tending to produce the finely dispersed or "hydrosol" condition of the particles, favors their passage through the filter. Thus a gold hydrosol with particles of 20–30 $\mu\mu$ and containing albumen, passed freely through a Pukall and a Maassen filter. In the absence of the protective albumen, the colloidal gold was adsorbed by the filter, gradually clogging the pores until the filtrate, at first red, became colorless. In technical practice, wherever possible, a coagulated precipitate is formed, whose large particles are held back with comparative ease. It is very difficult to filter glue or gelatin solutions or precipitates formed in the presence of protective colloids.

The successful treatment of sewage, backwaters and trade effluents depends largely upon the separation from them of colloidal impuri-

ties by coagulation, adsorption and filtration. The old ABC method depended upon the use of alum, blood and clay (whence the name) to make a coagulum which would carry down suspended matter. Ferrous sulphate and lime (yielding a coagulum of ferric hydroxid) and alum are also used as clarifiers and coagulants. Filtration through sand, coke, etc., is made use of to adsorb finely dispersed impurities.

Animal charcoal and fuller's earth decolorize sugar and oils respectively, because of their powerful adsorptive action.

CHEMICAL ANALYSIS. — The presence of colloids, especially in technical products or solutions, may lead to grave errors in analysis, so that the chemist should destroy them by ignition, or else nullify their effects by the addition of a sufficient excess of coagulant or precipitant. Reversible colloids which are frequently referred to under the vague term "organic matter" may act: (1) by totally or partially preventing the formation of precipitates, just as tartaric acid and tartrates prevent the precipitation of alumina, chromic oxid, and ferric oxid (see Yoshimoto, J. S. C. I., 1908, **27**, 952); (2) by preventing the satisfactory

filtration of the precipitate formed (see Mooers and Hampton, J. Am. Chem. Soc., **30**, 805); (3) by rendering precipitates difficult to wash and purify (see Duclaux, J. S. C. I., 1906, **25**, 866).

A few experiments will serve to make clear the importance of these remarks. Three solutions of lead acetate were taken; to the first was added hydrochloric acid which yielded a heavy coagulated precipitate; to the second was added sodium chlorid (a less highly ionized precipitant) which yielded a colloidal precipitate of lead chlorid; to the third was added, first, a little glue solution and then sodium chlorid which in this case gave no precipitate at all.

Again in the presence of glue, silver nitrate gives with sodium chlorid only an opalescence which passes through filter paper. Even a large excess of hydrochloric acid fails to produce a precipitate. But upon adding silver nitrate solution to a chlorid solution containing no colloid, a copious precipitation occurs at once.

PHARMACY. — Colloids, such as gum arabic, Irish moss, tragacanth, etc., are largely used in pharmacy in the preparation of emulsions. If ferric chlorid be added to gum arabic emul-

sion of cod liver oil, it coagulates the gum, and the oil, no longer protected by the emulsostatic action of the gum, promptly separates out.

Colloidal silver (collargol, argyrol), colloidal mercury (hygrol, blue ointment), and colloidal sulphur (ichythol) are largely used medicinely. Ferric salts, especially the chlorid which readily hydrolyzes into the hydrate, act as styptics or hemostatics by coagulating the blood colloids. The action of disinfectants is largely controlled by colloid-chemical factors — the disinfectants are adsorbed by bacteria, and either coagulate their protoplasm or flock them out.

Foods and Their Preparation. — It is a serious error to judge foods upon the basis of a bald chemical or calorific analysis. Fat, protein, carbohydrate and calories are not alone the criteria of food value — the physical condition of food largely governs its usefulness to the organism. The experiences of centuries has taught us the value of "light" bread or cake, leavened by yeast or baking powder until it presents an enormous surface to the digestive juices; unleavened bread was

eaten only in time of stress, as we learn from the Bible. The meats yielded by young animals are more juicy and tender than those obtained from older animals, because the latter are formed from tissues partially dehydrated by age.

The ancient art of cooking involves many factors besides mere digestibility and assimilation; taste, flavor, odor and variety are important. Egg albumen when cooked is probably more slowly absorbed and loses its species-specificity; therefore, some people who have an idiosyncracy against raw eggs can eat cooked eggs. Cream is an emulsion of fat in an aqueous medium and *wets* paper; butter is an emulsion of water in a fatty medium and *greases* paper.

PHYSIOLOGY AND PATHOLOGY.—The changes which occur on almost all physiological processes are remarkable not only because of their very profound nature, but also because they are produced at comparatively low temperatures and in the presence of very dilute reagents. The living organism disintegrates proteins, oxidizes carbohydrates and with the same apparent ease synthesizes substances of

great complexity. Powerful reagents and high temperatures, which would be destructive to life, are necessary to bring about changes of this character under ordinary laboratory conditions.

The body and plant colloids (biocolloids) consist of carbohydrates (starch, cellulose, glycogen), proteins (plant and animal albumins), and lipoids (lecithin, cholesterin, fats and oils). Each tissue has a normal turgor or state of swelling which is greatly influenced by acids, alkalis and salts. The *swelling and shrinking* of tissues, together with their selective adsorption and the differential diffusion of solutions through them, account for or accompany many physiological phenomena, both normal and pathological. Thus, fibrin and gelatin swell much more in very dilute acid than in distilled water, but the swelling is depressed by salts. Fibrin is so sensitive that it swells in the presence of traces of acid quite undetectable by ordinary indicators, such as litmus; in fact fibrin itself is a most sensitive indicator.*

* Though the normal H ion concentration of the blood is 0.37×10^{-7}, a concentration of 1.00×10^{-7} nH represents an advanced acid intoxication.

Local accumulation of acid in the organism may cause swelling (edema); for example, insect stings, which may be imitated by stinging gelatin with a needle dipped in acid. If acid accumulates in an organ with a rigid capsule (eye or kidney), the swelling tends to establish a vicious circle (glaucoma, nephritis) by compressing the blood vessels and cutting down the alkaline blood stream, which is unable to wash out the acids (mainly CO_2) formed by living protoplasm.

If the oxidation processes of the body are normal, the hydrogen in foods is oxidized mainly to water and the carbon mainly to carbonic acid — a gaseous acid which is exhaled without demanding fixed alkali or protein of the organism for its elimination. It would require nearly two pounds of pure caustic soda to neutralize the acidity produced daily by an average man. In the case of pathological oxidation, however, other non-volatile acids are formed and a condition called "acidosis" may arise, which is in reality a diminished alkalinity, recognizable by the fact that an abnormally large quantity of bicarbonate of soda is needed to render the urine alkaline.

These acids may cause disturbances of the body colloids, disease and even death. In fact, throughout life there is a gradual syneresis of the biocolloids accompanied by visible shrinking and loss of water — compare the chubby hand of a child with that of an old man. In plants an analogous process occurs in lignification.

DIGESTION. — The digestive process is preliminary to the actual adsorption and use of food by the organism, and has for its object the modification or change of the ingested food into such forms or such substances as may be absorbed in the lower part of the digestive tube. To have a correct understanding of the absorption of the products of digestion, we must bear in mind the fact that the walls of the digestive tract act as semipermeable colloid membranes and that absorption involves diffusion into or through these membranes or their constituent cells. Substances in crystalloidal solution, and colloidal sols whose particles are sufficiently small, represent then the two classes of digestion products which are diffusible and therefore absorbable.

Food as ingested consists mainly of sub-

stances that may be grouped into two classes:

1. Crystalloids — such as water, sugars, sodium chlorid, etc.

2. Colloids — such as starch, proteins, emulsions, etc.

The crystalloids in foods are usually absorbed directly, although sucrose, for example, undergoes inversion. The colloids, as a rule, are not directly absorbable, and, for the most part, digestion consists in the disintegration of the colloidal complexes of the food, so that they can actually diffuse into the organism and there undergo further changes. Colloidal gels or even sols whose particles are of large size are, practically speaking, non-diffusible, and must, therefore, be reduced to a more finely dispersed state.

Investigation has demonstrated that the high efficiency of the digestive juices is mainly due to small quantities of certain colloidal substances called enzymes (such as ptyalin, pepsin and pancreatin) which act as catalyzers, enormously hastening reactions which would otherwise proceed so slowly that, practically speaking, they would not occur at all. The enzymes appear to act by forming with the

substrate a combination of unstable character, which breaks down and liberates the enzyme again to continue the operation. Recently W. M. Bayliss, in his interesting monograph on "The Nature of Enzyme Action," has shown that in all probability "the compound of enzyme and substrate, generally regarded as preliminary to action, is in the nature of a colloidal adsorption compound." Anyone who has seen in the ultramicroscope the extremely active motion of the individual particles in colloidal solutions, can readily imagine the terrific bombardment a substance must undergo when a colloid enzyme is concentrated on its surface by adsorption, and indeed it seems probable that enzymes actually produce their effects by virtue of their specific surface actions and the motion of their particles.

In order to find out if this idea could be verified by actual observation, the author watched under the ultramicroscope the action of diastase upon potato starch grains and the action of pepsin upon coagulated egg albumen.

In the first case, actively moving ultramicrons in the diastase solution gradually accumulated about the starch grains, which

after a time showed a ragged and gnawed margin. While the adsorption and motion of the larger ultramicrons was all that could be followed, the bright appearance of the field indicated that more numerous finer particles were present, and some apparently of intermediate size were seen.

For observations on albumen there was used a dilute solution of white of an egg which has been heated nearly to boiling. It was opalescent and in the ultra apparatus exhibited a field full of bright and rapidly moving ultramicrons. Upon allowing a droplet of essence of pepsin (Fairchild's, containing 15 per cent of alcohol by weight) to diffuse in, an immediate coagulation occurred, the particles clumping into very large masses. A droplet of decinormal hydrochloric acid was then allowed to diffuse in, whereupon the large masses broke up in small groups and single ultramicrons, which once more resumed their original motion. Soon, however, the albumen particles began to grow smaller and disappear, the field all the while becoming brighter and brighter, indicating the concommitant appearance of smaller ultramicrons or amicrons. *In vitro* the addi-

tion of the pepsin to the opalescent albumen solution caused it to clear gradually, even at room temperature.

Enzymes are inactivated to a greater or less extent by shaking, heating, electrolytes, etc., all of which, as is well known, cause the coagulation of colloidal solutions and a resulting decrease in the activity of the motion of their constituent particles. Another feature of interest is that the action of enzymes is reversible, a fact that does not come much into evidence because of the dilution and removal by diffusion of the products formed. In cells, tissues and organs, however, changes of concentration again occur and synthetic processes may result.

One principle of colloid chemistry is of the utmost importance in digestion, namely: the protective action of reversible colloids, which stabilize or protect from coagulation irreversible or unstable colloids. Mucin and analogous colloidal substances undoubtedly have a function of this character, which may in some cases account for the variance between the action of natural and artificial digestive juices. The effects of colloidal protection are in

evidence in almost all physiological reactions and processes, and it is indeed extremely doubtful if there ever occurs *in vivo* any chemical reaction which is not greatly influenced by the colloids always present.

ABSORPTION, SECRETION AND EXCRETION. — These are largely affected by the swelling and shrinking of the body colloids and by selective adsorption and differential diffusion. It must be remembered that the blood is in reality a circulating fluid colloid, whose attraction for water is greater in the "acid" or venous condition, than it is in the "alkaline" or arterial condition. Tissues and organs well supplied with venous blood tend to adsorb water (intestine); whereas those well supplied with arterial blood tend to give up (secrete or excrete) water (kidney); and as the blood is passing in a continuous stream, the process continues as long as the water supply permits and until the blood is in equilibrium with the other tissues.*

* The functioning of organs is largely controlled by nervous influences. Thus a sudden nervous shock may by vaso-dilation send an excessive supply of arterial blood through the mesenteric arteries (an "internal blush"), and result in a secretion of fluid into the intestine (nervous diarrhea).

Conditions which decrease the capacity of the blood and tissues to hold water (diuretics, hyperglucemia and acidosis in diabetes) naturally result in the elimination of the excess or "free" water (polyuria, diarrhea).

Minute quantities of acid increase the swelling capacity of colloids, which quickly reaches a maximum; after which increasing acidity causes shrinking. Neutral salts oppose the action of acids apparently by driving back the ionization of the acid and thereby reducing the H-ion concentration which is the controlling factor.

The action of selective adsorption and differential diffusion in effecting secretion and excretion must be at once manifest. Easily hydrolyzable compounds may be thus split up in the body, and yield secretions of acid nature like the gastric juice, or of alkaline nature like the pancreatic juice, depending upon the structure of the organ, the location of its cavity and of its afferent and efferent vessels. Individual compounds in the blood stream or other body juices may also be selectively diffused out, concentrated or separated from other accompanying substances. By selective

adsorption, circulating substances may be fixed and taken from the circulation; in fact, poisons are usually taken up selectively by certain organs and tissues.

An insight into the mechanism of body processes may be obtained by considering the

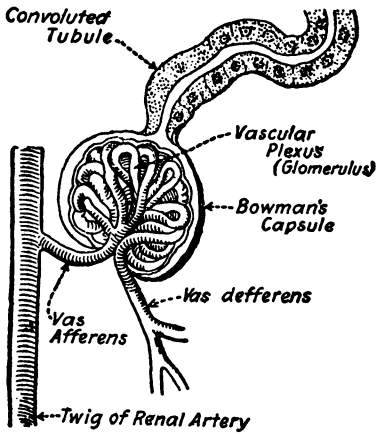


FIG. 1. Glomerular structure.*

functioning of the kidney (see Fig. 1). The Malpighian tufts are plentifully supplied with arterial blood having "free water," and

* From Dr. J. G. M. Bullowa's translation of Bechhold's "Colloids in Biology and Medicine," D. Van Nostrand Co., 1919.

under the pulsating pressure* of the blood stream, they ultrafilter off a very dilute but copious blood ultra-filtrate into the long convoluted tubules. The tubules, however, are plentifully supplied with venous blood, which is unsaturated with water and which therefore reabsorbs most of the water together with some of the dissolved substances contained in the preliminary excretion; so that there drips into the pelvis of the kidney a concentrated urine having in solution many of the substances found in the blood, but in a much higher concentration. Bechhold estimates that the average of two liters of urine voided daily by an average man, represents a preliminary excretion of fifty liters, of which forty-eight are reabsorbed within the kidney itself.

In plants, differential diffusion and selective adsorption seem to be intimately bound up with growth and the circulation of the sap. The plant tissues are mainly colloidal gels or finely integrated structures, and as the sap circulates or diffuses through them, each tissue

* Since the vas defferens has a smaller lumen than the vas efferens, a "back pressure" is created within the Malpighian tufts.

selectively adsorbs and elaborates certain particular constituents. Thus with the potato and tapioca plants the starch forming substances are fixed in the roots; with the sago palm they are fixed in the stem pith; and with cereal grains, in the seeds. As long as the adsorptive tissues are unsaturated or are multiplied, so long can growth continue, the stem and branches taking up the substances required for the upward growth, and the root taking up those required for the downward growth.

When we consider the great variety of biocolloids and their susceptibility to changes of structure and diffusive or adsorptive capacity, we can easily understand the almost infinite number of reactions that may go on within their recesses, as they swing the balance of the law of mass action over particles reduced to a reactive degree of subdivision.

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